

Session 3 : Conversion and Fuel Fabrication

Multiparametric study of hydrothermal conversion of uranium (IV) oxalate



Jérémie Manaud

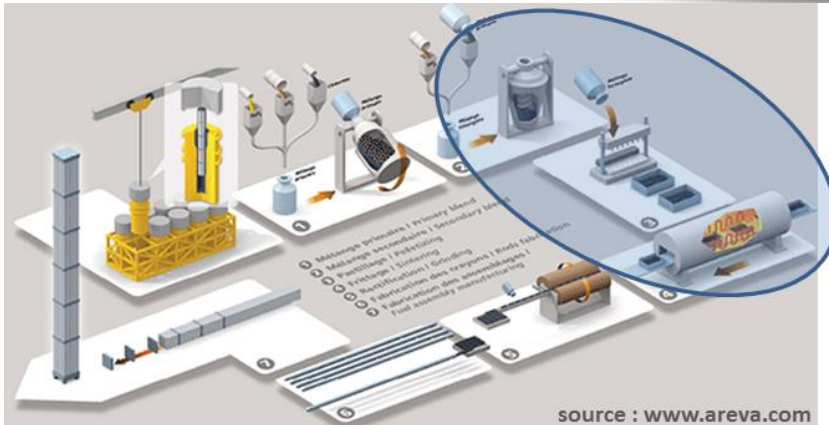
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***Materials Interfaces in Evolution Laboratory (LIME)
Hybrid systems for Separation Laboratory (LHyS)***



École Doctorale
Sciences Chimiques Balard



MOX fuel fabrication process :

Powder metallurgy with UO_2 and PuO_2

Shaped by uniaxial pressing

Sintering → Thermal treatment :

$T \sim 1700^\circ\text{C}$ / $t \sim 4$ hours

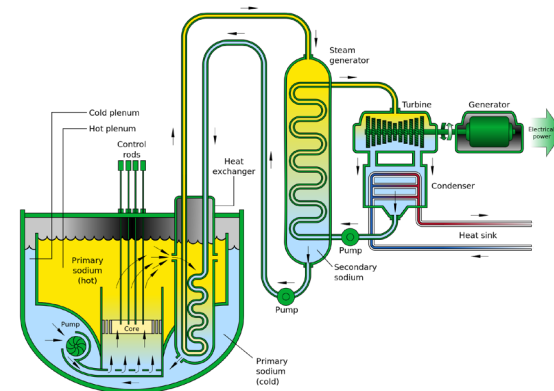
Reducing atmosphere

Technological challenges :

Gen(IV) development : increase of the plutonium amount

Enhance the resistance to proliferation

Need to develop / optimize fabrication processes



➤ Development of wet chemistry routes

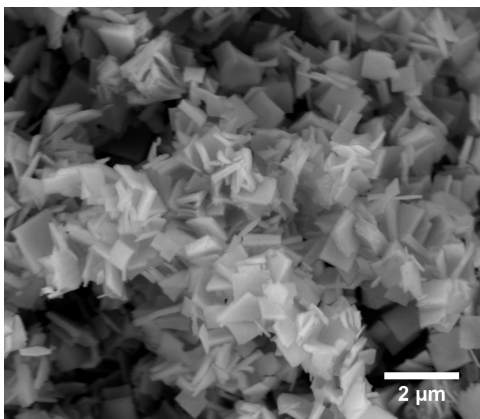
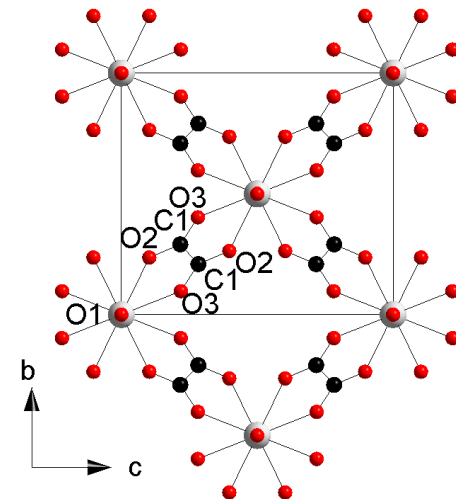
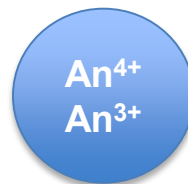
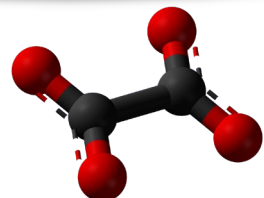
Actinide oxalates :

Compounds studied for more than a century

Quick and quantitative precipitation of cations

Very rich crystal chemistry

Pseudomorph conversion into oxide under thermal treatment



Potential drawbacks :

Need of a **thermal conversion** step towards dioxide

Presence of **residual carbon** in oxide phases

Morphology often poorly adapted to the sintering

Avoid thermal conversion step

Direct precipitation of An hydrated oxides from solution

Optimisation of carbon elimination in solution

Control aggregation / assembly of nanocrystallites

Hydrothermal conversion of uranium(IV) oxalate



Temperature



pH

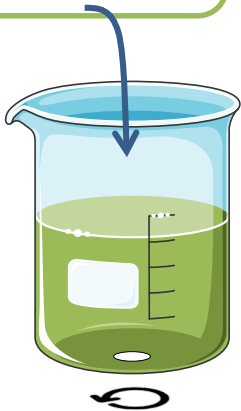


Kinetics

Hydrothermal conversion of uranium oxalates



U(IV) in HCl (6M)
+ Oxalic Acid (excess)
+ HCl



$V_{TOT} = 15\text{mL}$
 $\text{pH} < 1$

Formation of **uranium oxalate precipitate**
 $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$

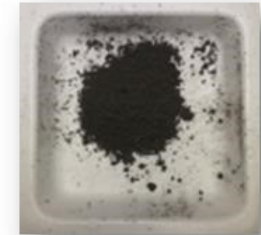
Hydrothermal
Treatment



$\text{RT} < T < 250^\circ\text{C}$
 $t = 24\text{h}$

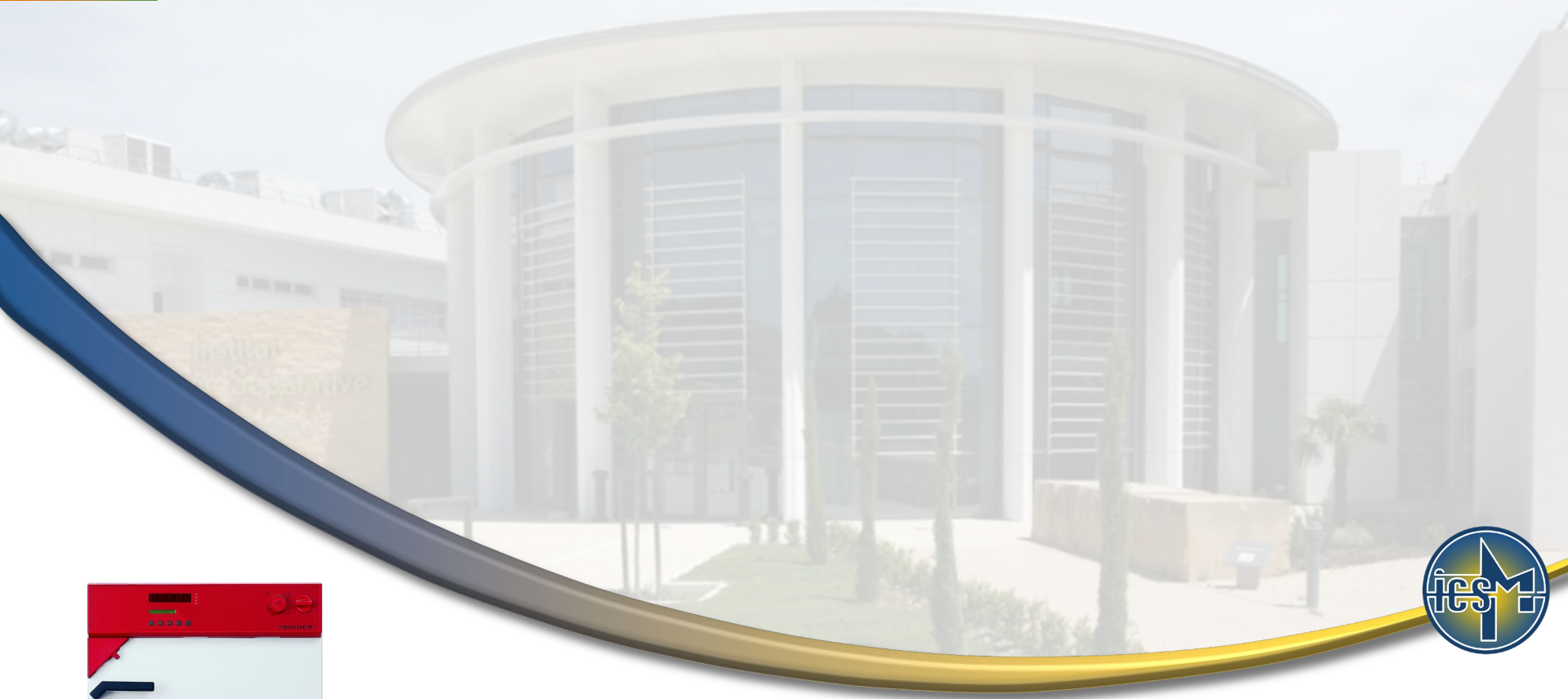
Washing

Drying at
 90°C



Powders characterisation :

- **Structural** (XRD)
- **Morphological** (SEM)
- **Chemical** (C content)

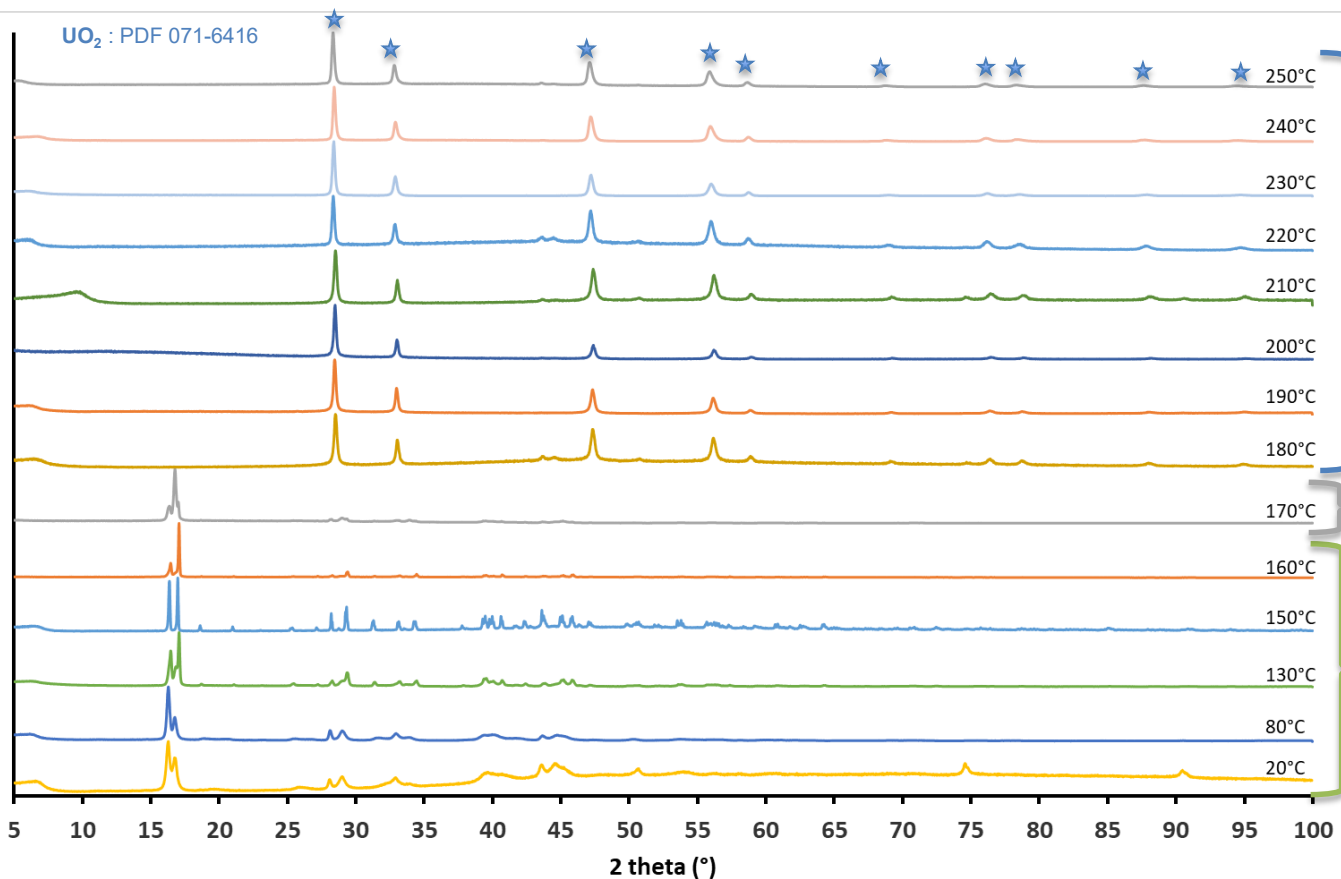


Temperature effect

XRD diagrams vs T



pH < 1
t = 24h



180°C ≤ T ≤ 250°C :
UO_{2+x}, nH₂O

T = 170°C :
**U(C₂O₄)₂, 2H₂O +
unknown structure**

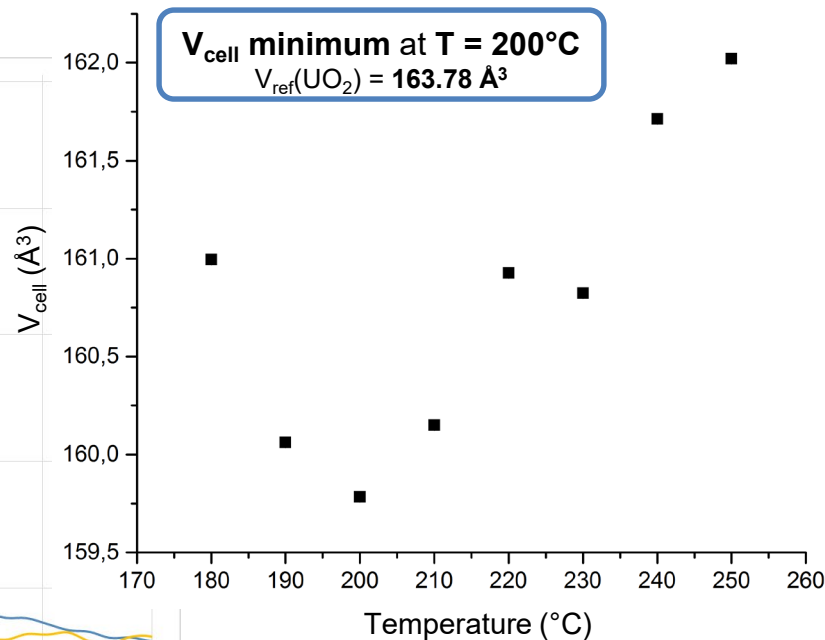
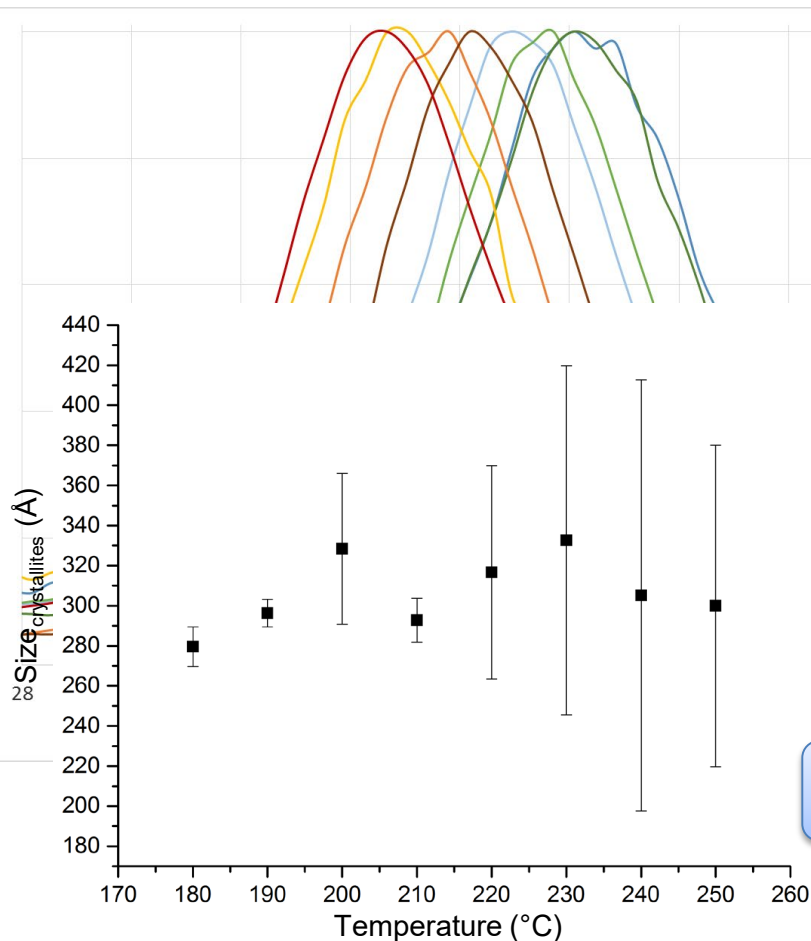
RT ≤ T ≤ 160°C :
U(C₂O₄)₂, 2H₂O

Rietveld refinements vs T



pH < 1
t = 24h

Rietveld refinements



O/M ratio or C/H₂O amount ?

Increase of the error bar →
strain inside structure

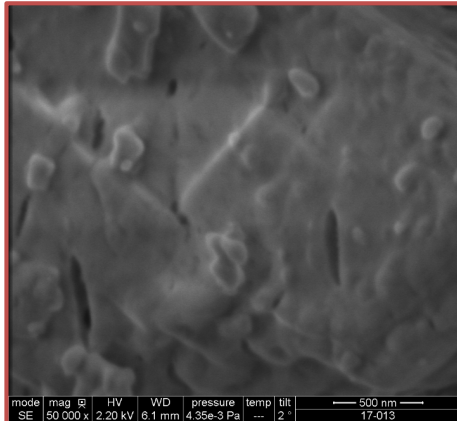
SEM vs T



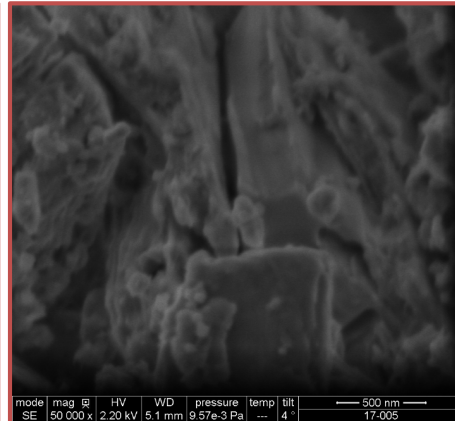
pH < 1
t = 24h

Oxalates as platelets

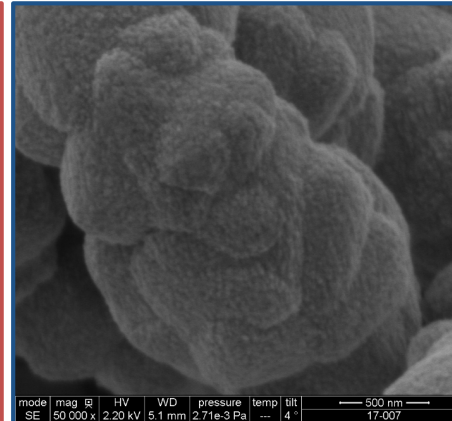
160°C



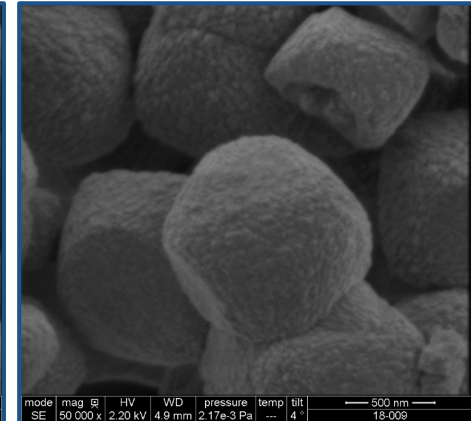
170°C



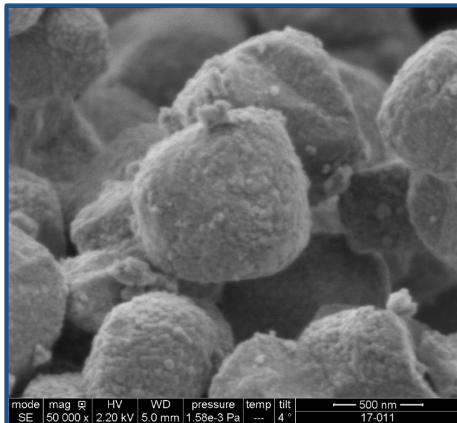
180°C



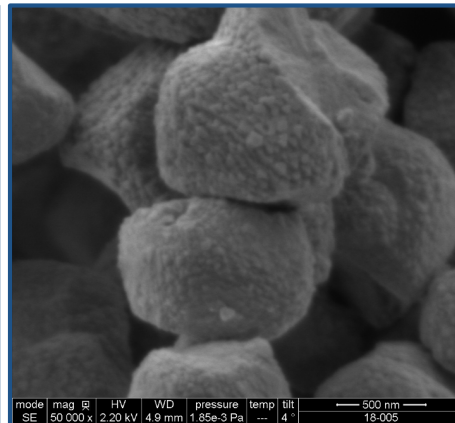
190°C



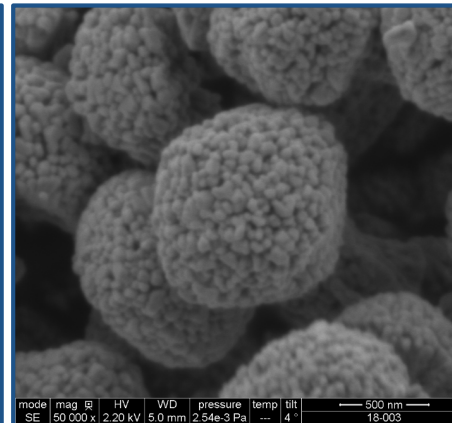
200°C



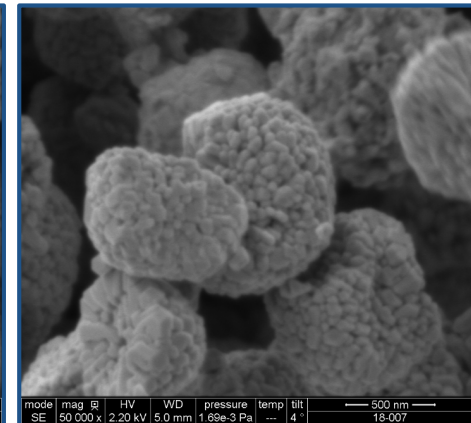
210°C



220°C



250°C



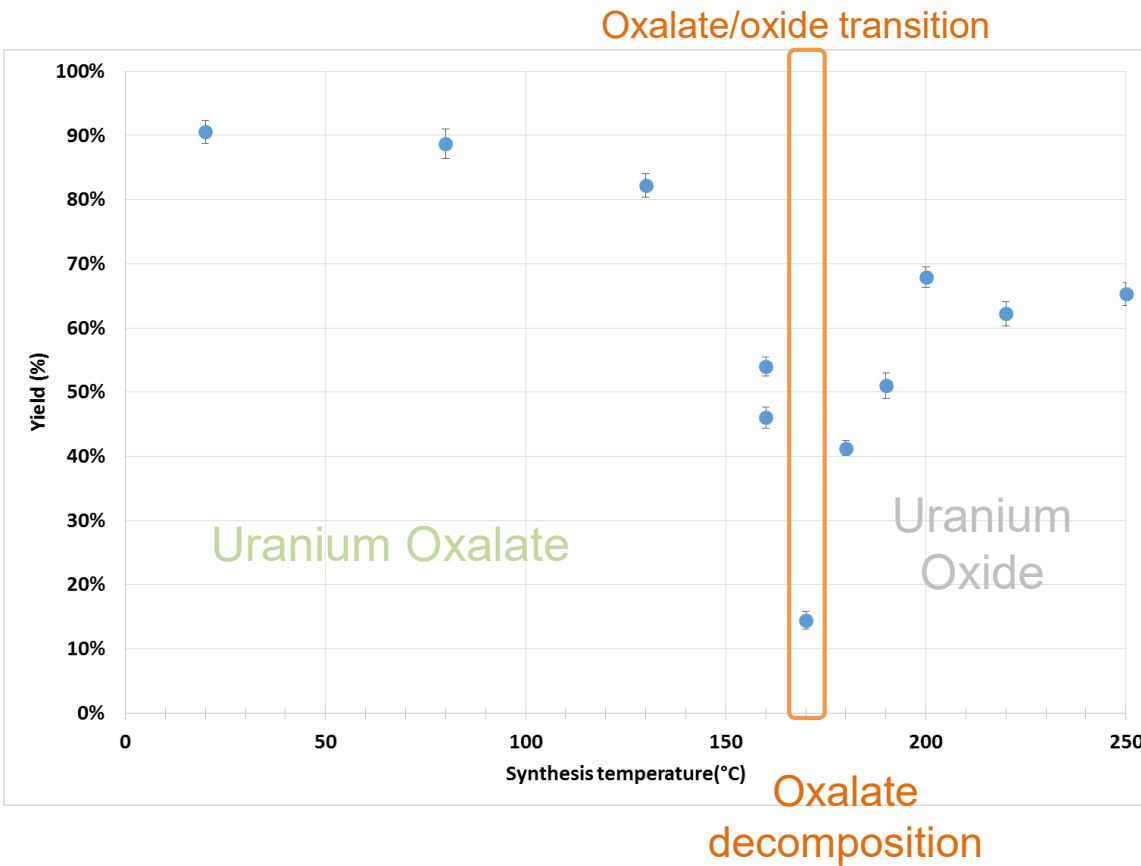
Oxides as ovoids

Precipitation yield vs T



pH < 1
t = 24h

Data from
**Photon
Electron
Rejecting
Liquid Alpha
Spectroscopy
(PERALS)**



Partial precipitation of
U(IV) → hydrolysis ?

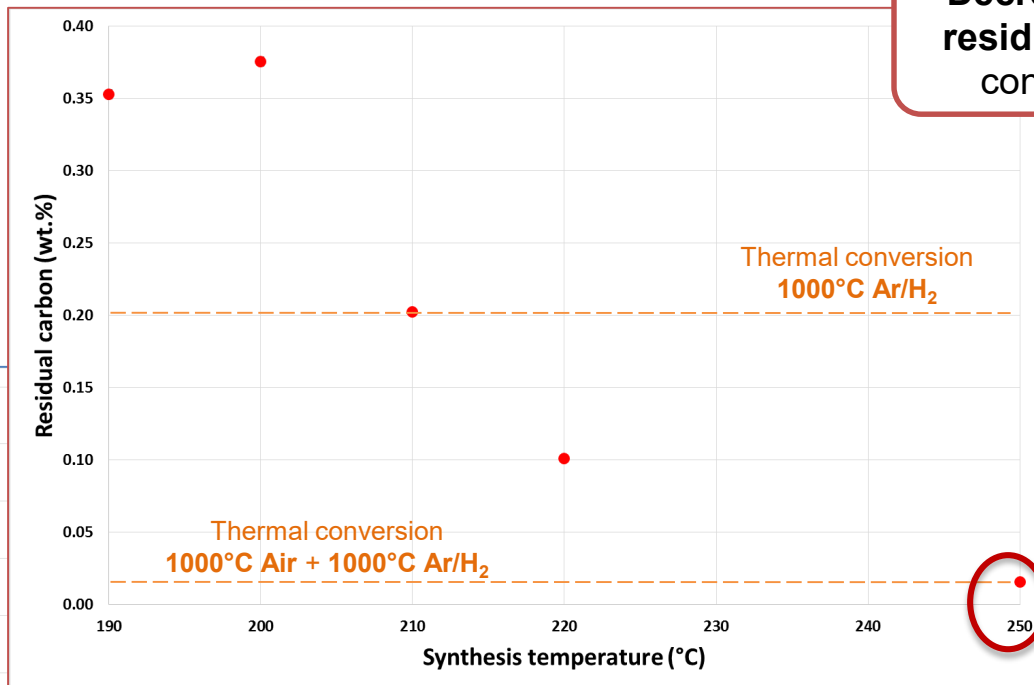
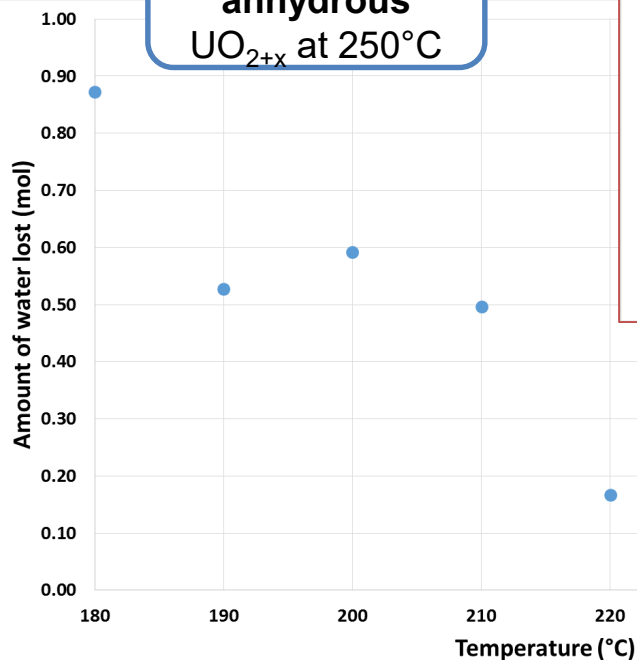
- **Decrease in yield** observed at the **oxalate/oxide transition**
- **Low yield** because of **low pH** → Ongoing study

TGA-MS and Carbon analyser vs T



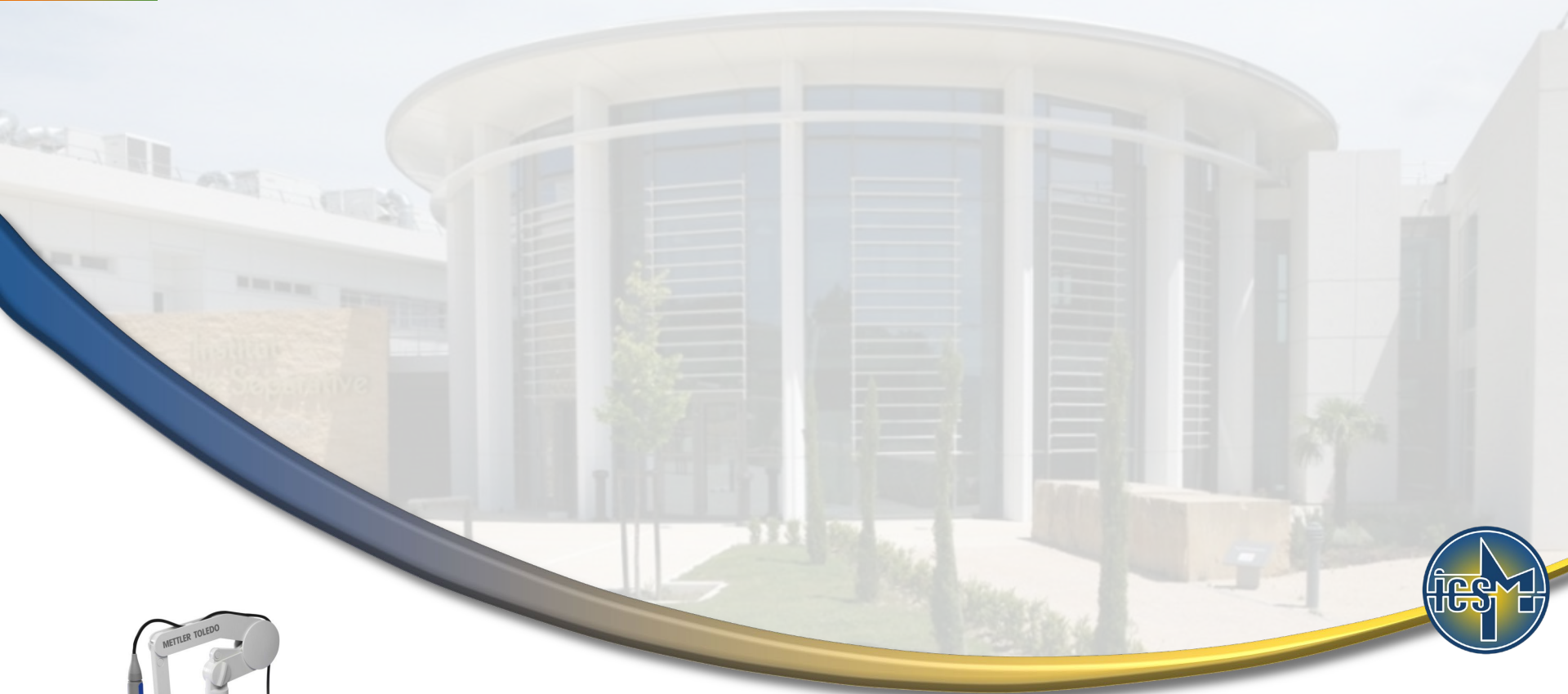
pH < 1
t = 24h

Almost
anhydrous
 UO_{2+x} at 250°C



Decrease of the
residual carbon
content vs T

**T = 250°C ; t = 24h and pH < 1
→ UO_{2+x} with very low amount
of residual carbon and water**



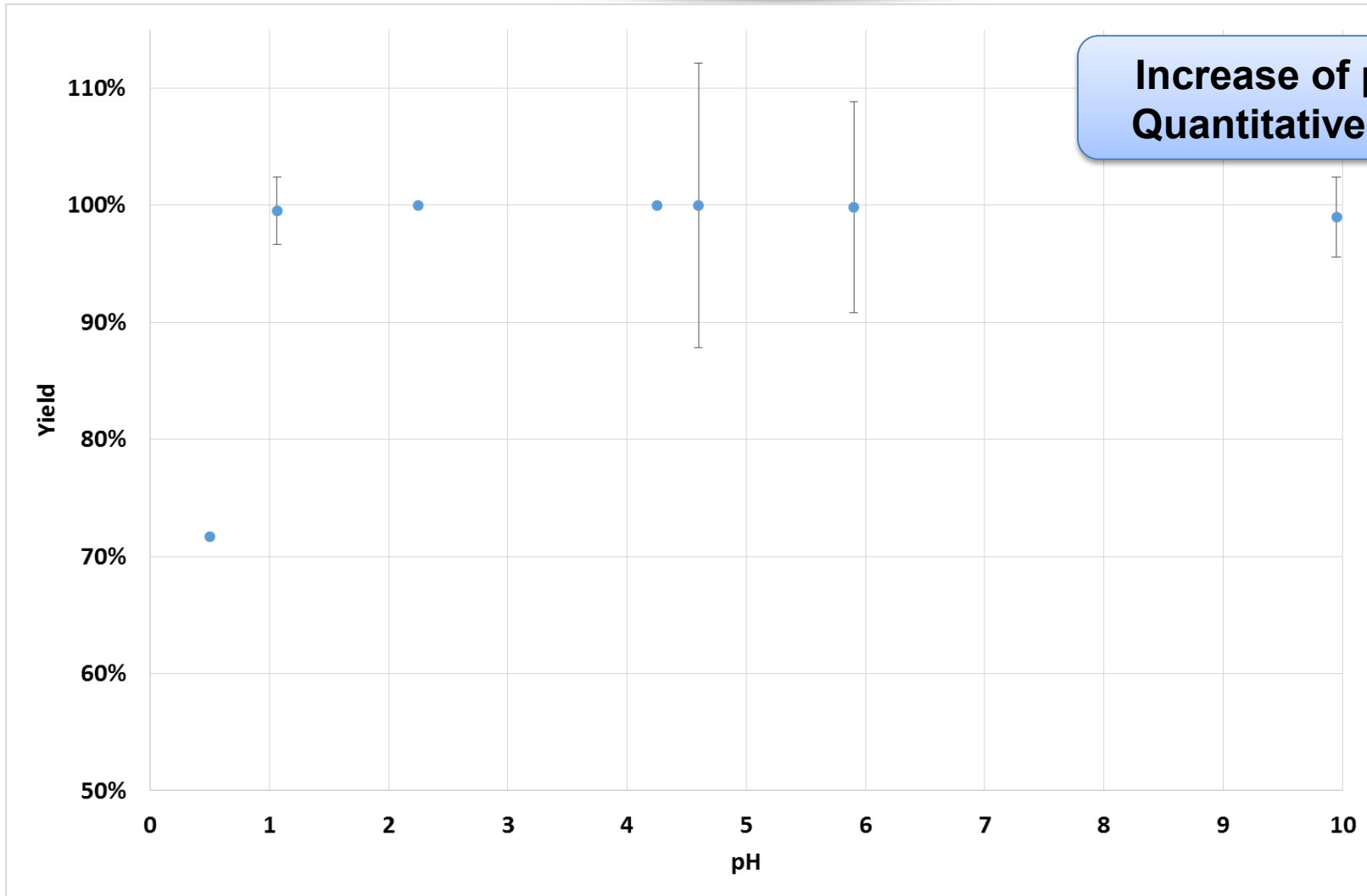
Effect of the pH

Precipitation yield vs pH



$T = 250^{\circ}\text{C}$

$t = 24\text{h}$



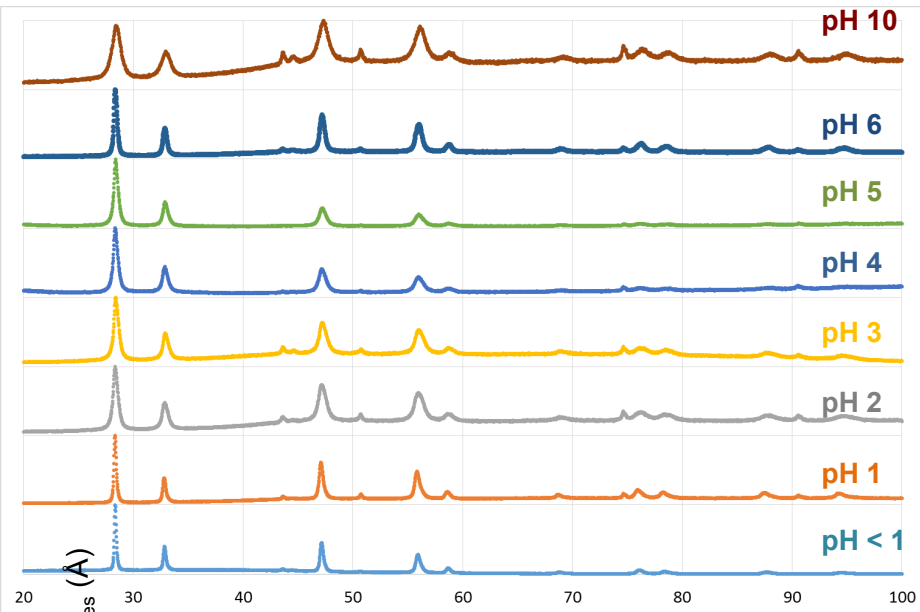
Increase of pH →
Quantitative yield

Rietveld refinements vs pH



T = 250°C

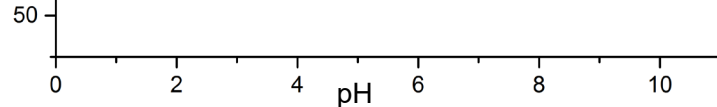
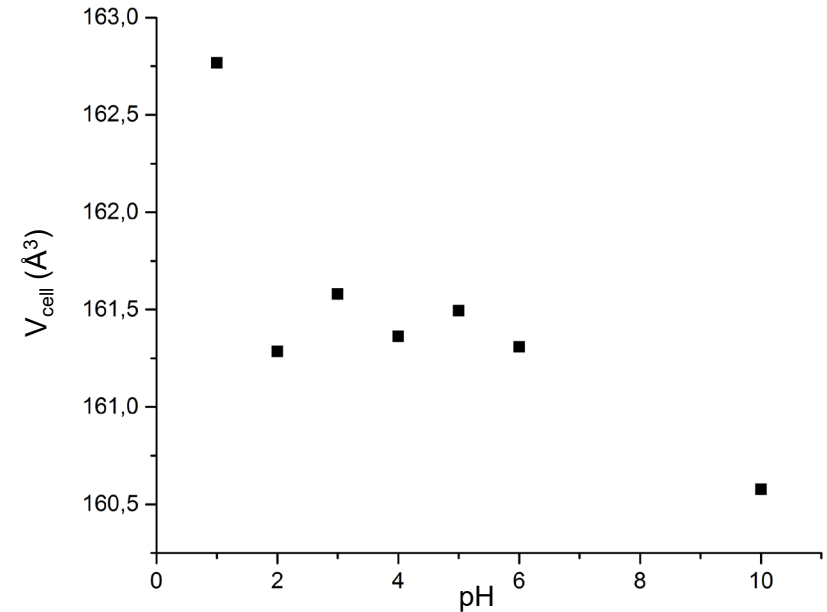
t = 24h



Size crystallites (Å)

Uranium dioxide formed for all pH at 250°C
 $\text{UO}_{2+x} \cdot n \text{H}_2\text{O}$

Increase of pH favoured
nucleation vs growth



T = 250°C

t = 24h

Morphology tends to **sphere-like** from pH<1 to pH 5

From **pH 2 to 5**, mix of aggregation states
+ many sizes of aggregates

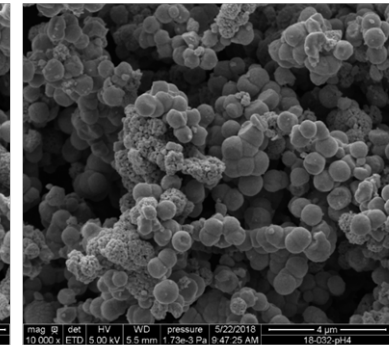
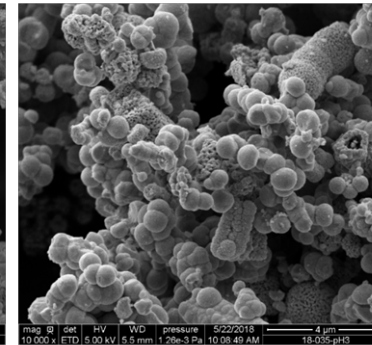
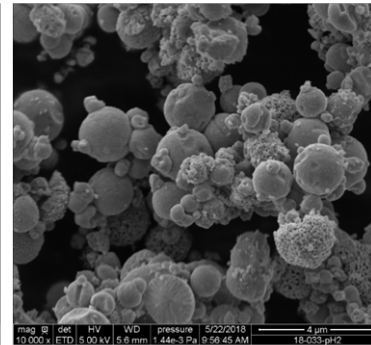
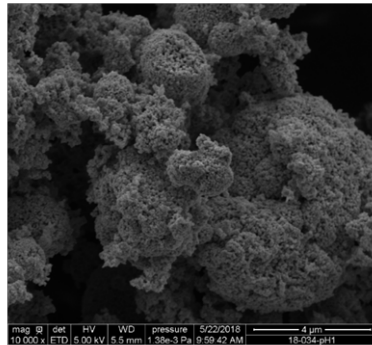
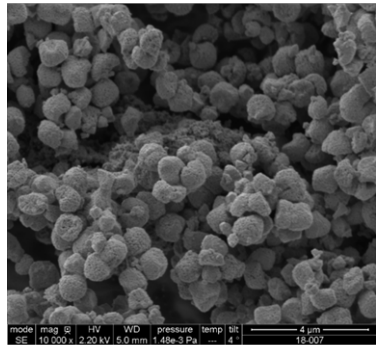
pH <1

1

2

3

4

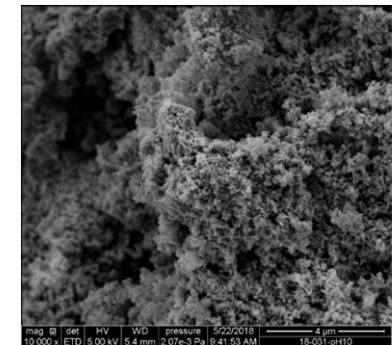
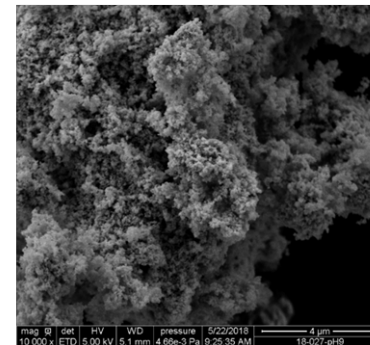
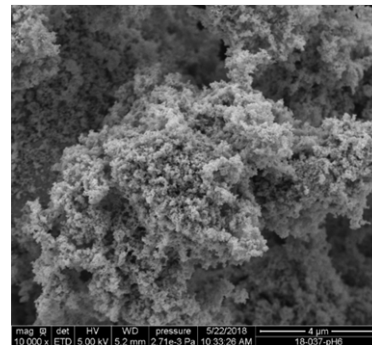
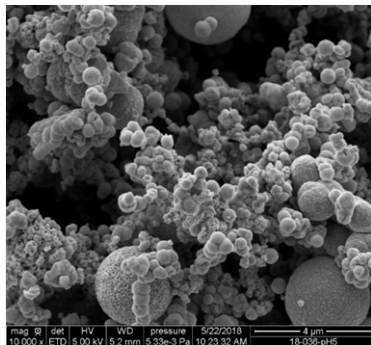


pH 5

6

9

10

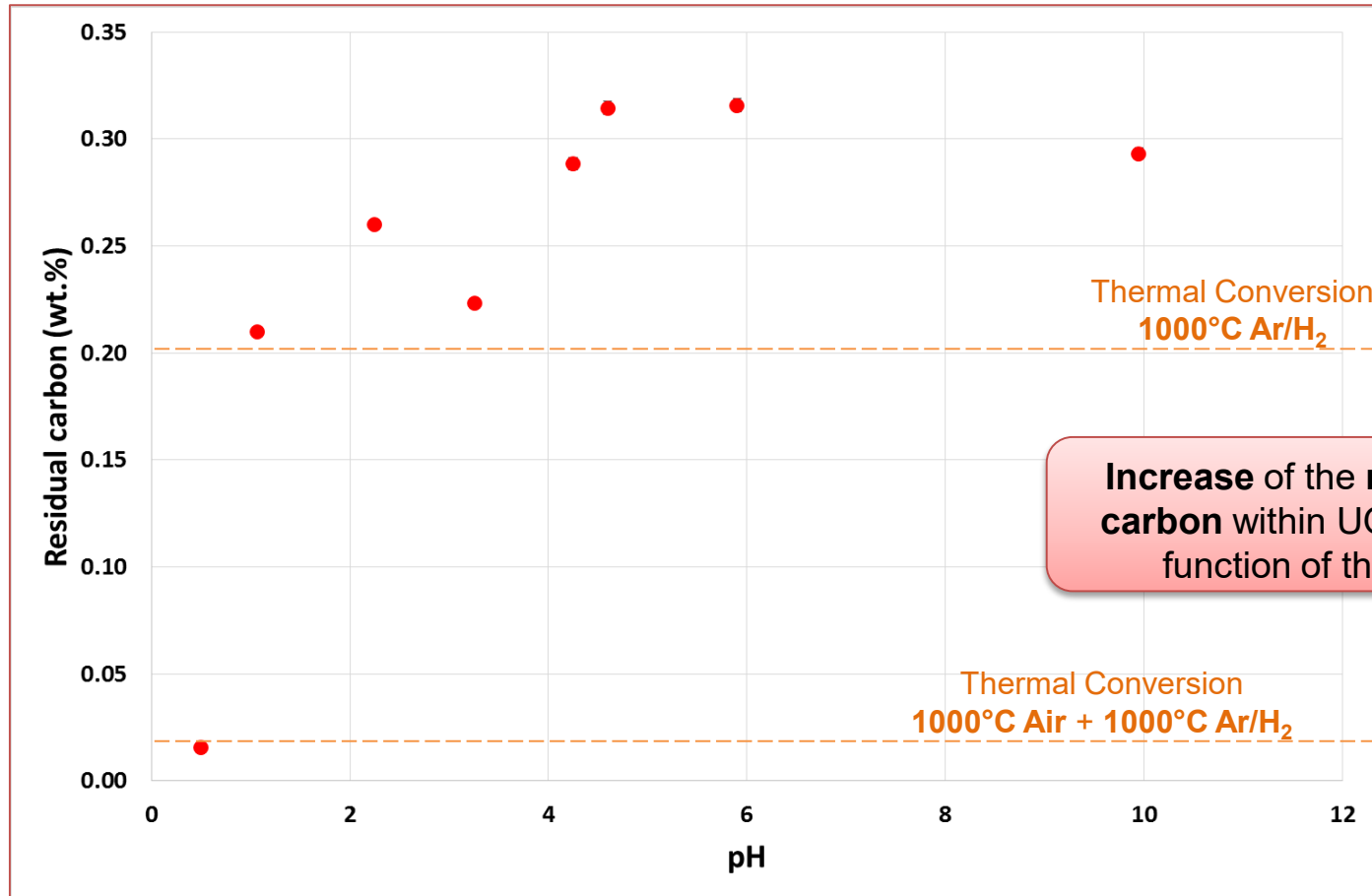


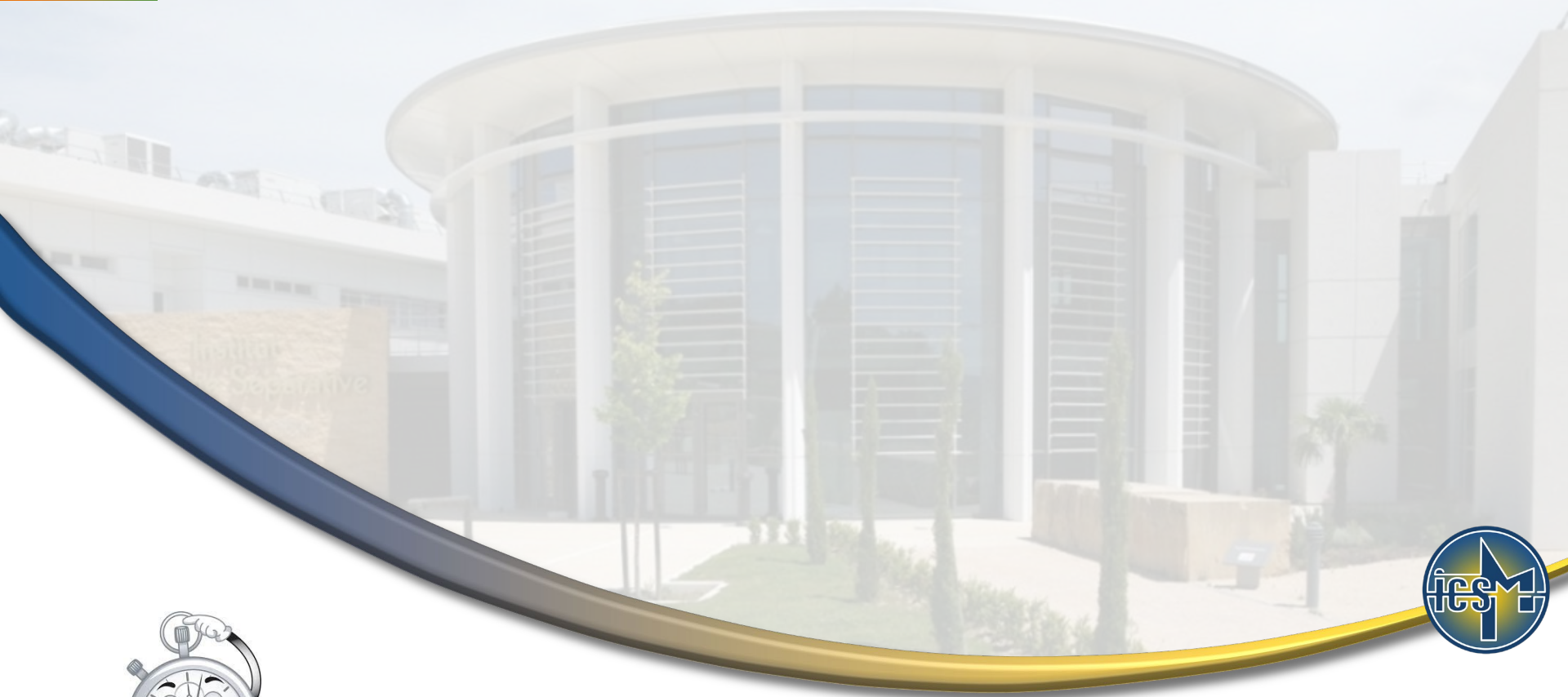
From **pH 6 to 10**, morphology
without particular shape

Carbon analyser vs pH



T = 250°C
t = 24h





Effect of the kinetics

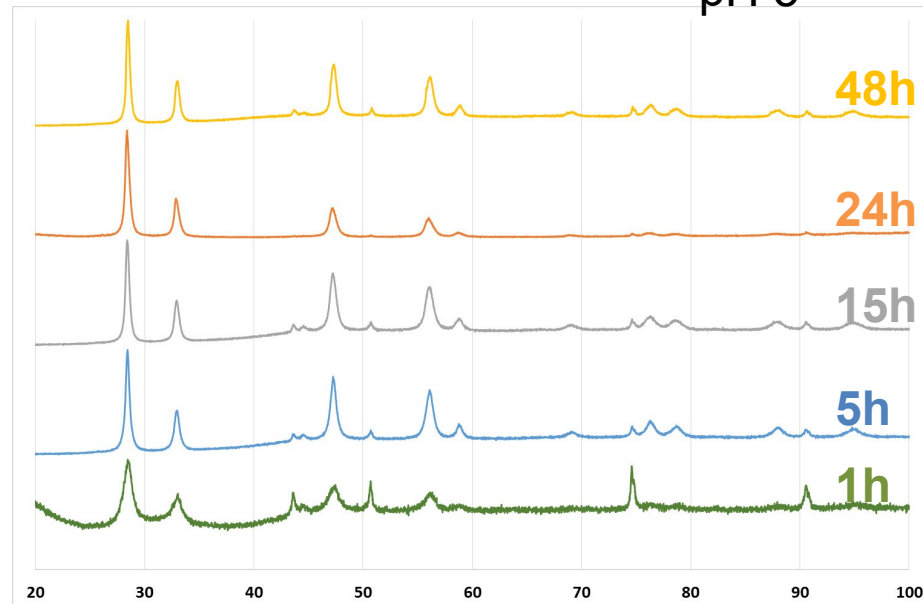
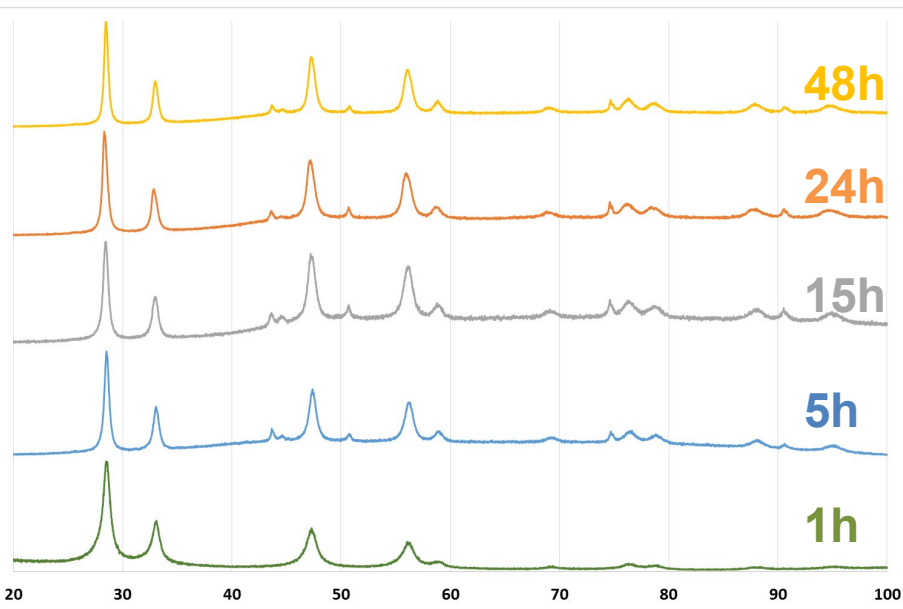
XRD vs kinetics



T = 250°C
pH 5

- No difference between the two pH studied
- Larger diffraction peaks after 1h
→ **Rietveld refinements under progress**

T = 250°C
pH 2



UO₂ : PDF 071-6416

UO_{2+x}, n H₂O synthesized by
hydrothermal treatment in only **1 hour**

UO₂ : PDF 071-6416

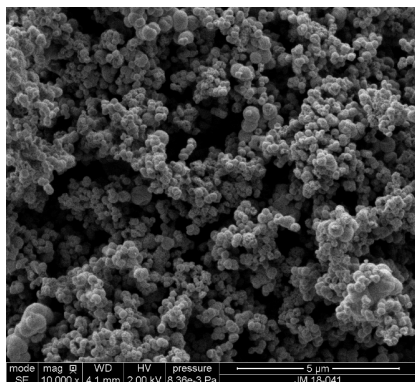
SEM vs kinetics



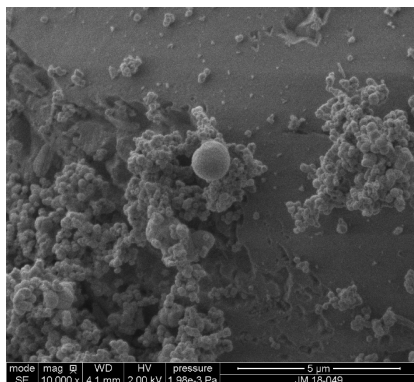
T = 250°C

pH 2

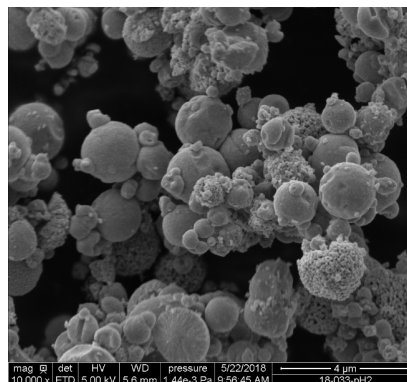
5h



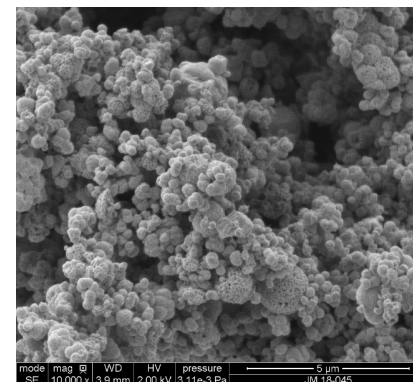
15h



24h

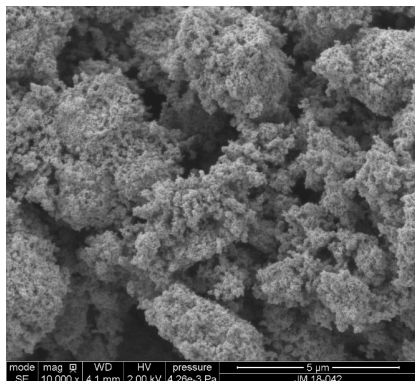


48h

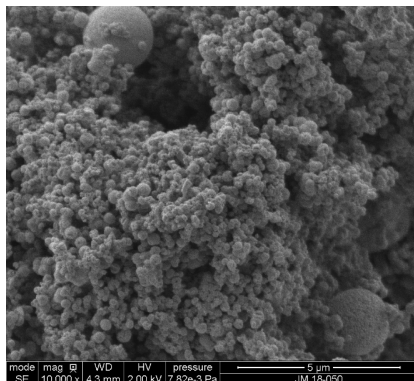


pH 5

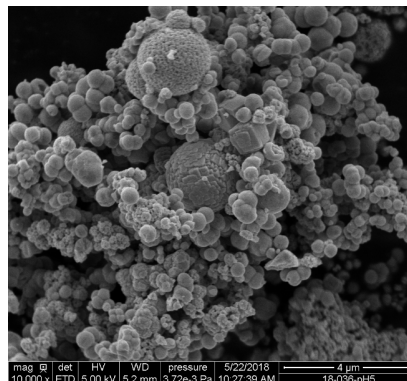
5h



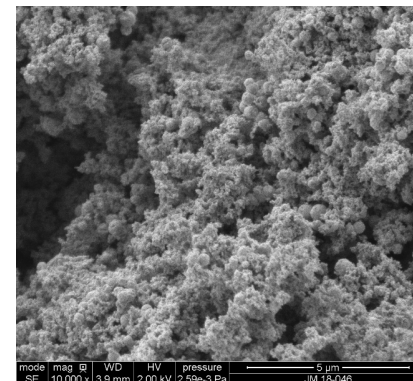
15h



24h



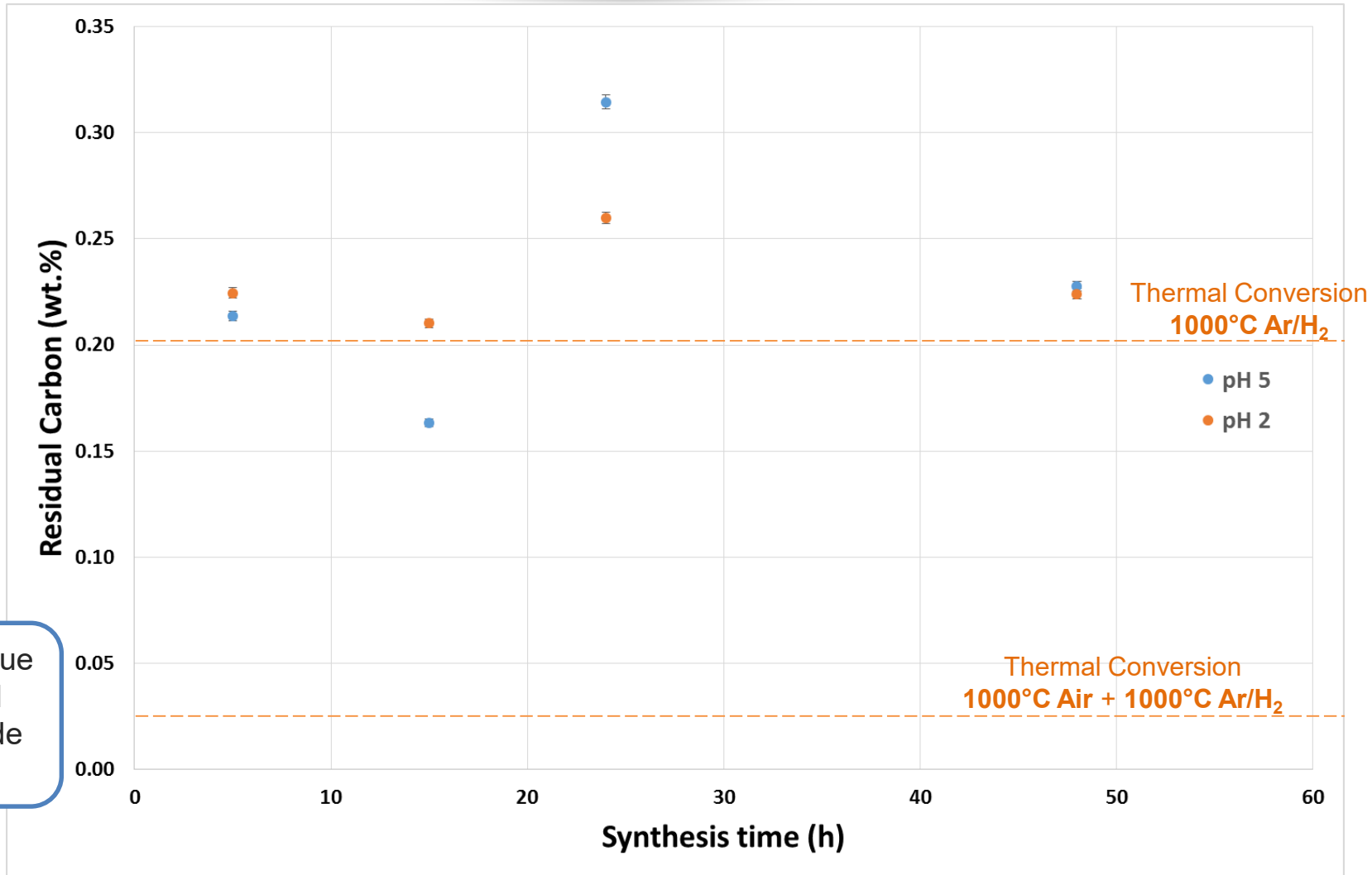
48h



Carbon analyser vs kinetics



T = 250°C

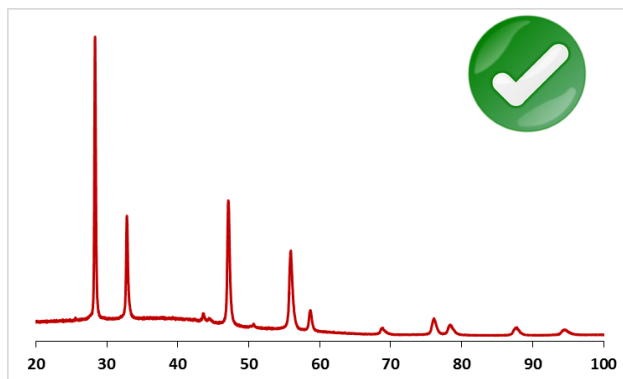


Conclusion

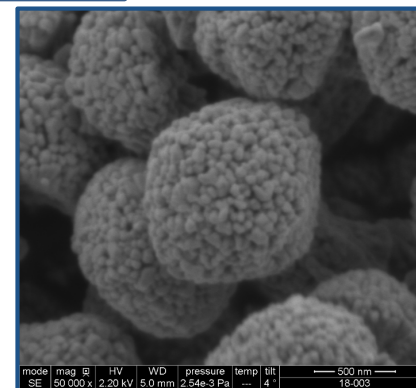


Hydrothermal conversion

$180^{\circ}\text{C} \leq T \leq 250^{\circ}\text{C}$
 $\text{pH} \leq 10$
 $1\text{h} \leq t \leq 48\text{h}$



Morphology



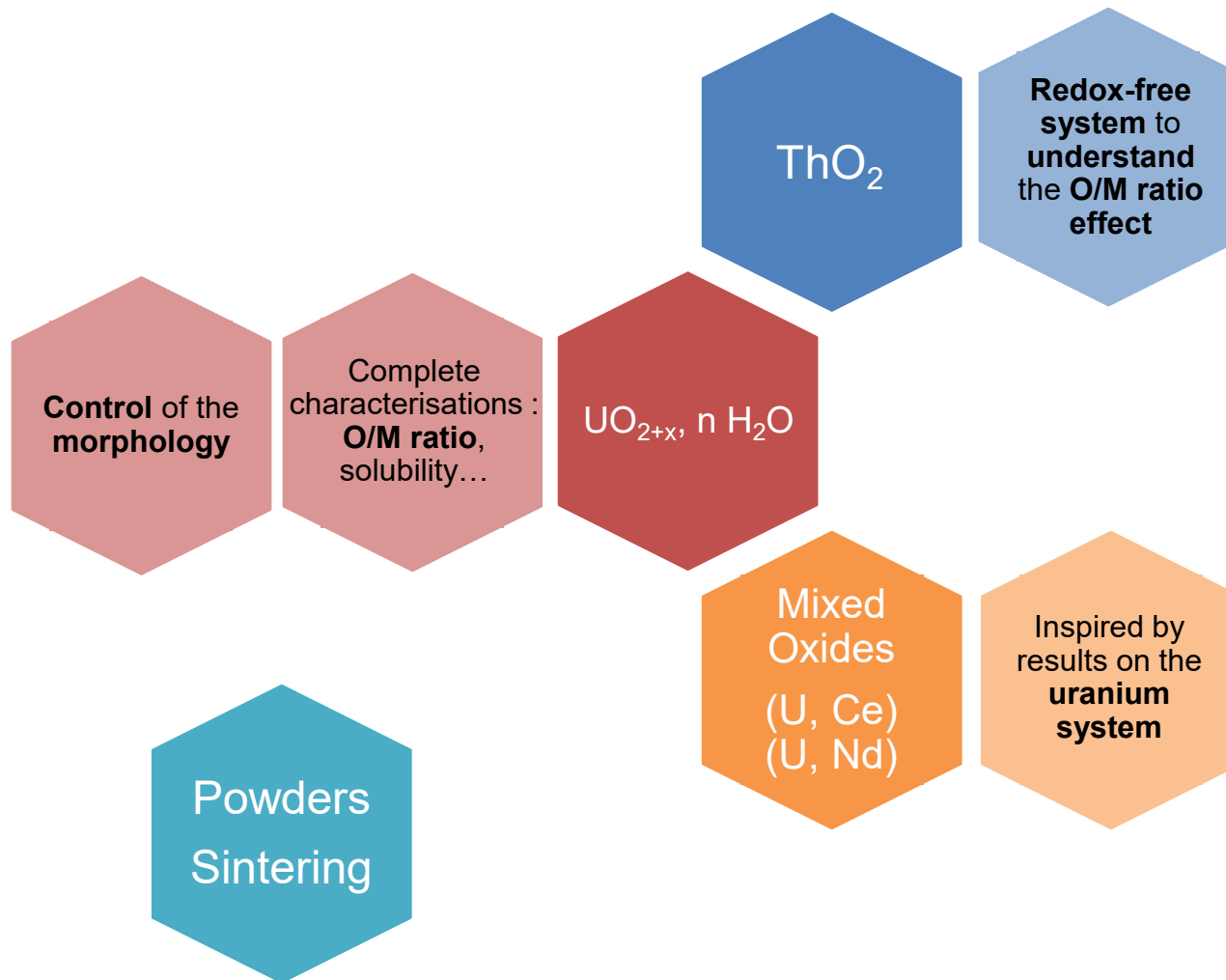
Precipitation yield

Quantitative
yield for $\text{pH} \geq 1$

Residual carbon / H_2O

0.02 wt.% of C
at **250°C**

0.1mol of $\text{H}_2\text{O}/\text{UO}_2$
at **250°C**





Thank you for your attention